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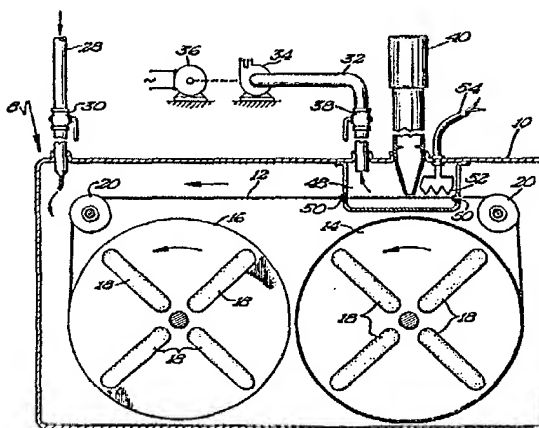
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54 Gas chromatograph/mass spectrometer interface.

57 Metal tape 12 is transported through a sample housing 48 from reel 14 to reel 16. Effluent from the gas chromatograph enters through vacuum connector 40 and the sample components are frozen onto the tape 12 while the carrier gas is removed through pump 34. The tape is kept cold by immersing the cassette 8 in liquid nitrogen. The housing 48 can be kept warm by heater 52 to prevent desposition of sample on the housing. A purge gas is introduced through valve 30 to prevent contamination by the carrier gas.

For transfer of the sample components to a mass spectrometer the valve 30 is closed and the housing pumped out to a high vacuum. The heater 52 is then used to evaporate the sample components from the tape, the speed of tape transport being matched to the scanning speed of the spectrometer.



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GAS CHROMATOGRAPH/MASS SPECTROMETER INTERFACE

The present invention relates to the preparation of a mass spectrometer sample from the effluent of a gas chromatograph.

5 Gas chromatography is very useful as a separator of compounds, while a mass spectrometer is an excellent instrument for identifications. An effective interface would allow each instrument to operate in
10 sequence, without degrading the performance of either. By separating the components of a specimen in a gas chromatograph, more accurate determinations with a mass spectrometer appear possible. However,
15 interfacing a gas chromatograph with a mass spectrometer presents two problems: (1) separation of the sample from the chromatograph carrier gas; and (2) the time between the different chromatograph peaks as they reach the mass spectrometer as compared to the necessary or desired scanning time of the
20 spectrometer.

The first problem noted above arises from the fact that gas chromatographs normally operate at pressures greater than 760 torr, while mass spectrometers function best at high vacuums in the
25 10^{-5} torr range, or greater. Fourier Transform mass spectrometers operate optimally near 10^{-8} torr. Thus, an interface between a gas chromatograph and a mass spectrometer has required a "throwing away" of some or most of the sample, with the
30 resultant loss of sample size sensitivity. This problem is even more pronounced with packed column

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gas chromatographs due to the higher quantity of carrier gas in the column which must be removed before the sample can be introduced into the mass spectrometer.

05 The customary approach for overcoming the problems due to the pressure differences between the two instruments is to separate the carrier gas from the sample. Conventional methods of separating the carrier gas include: effluent splitting or Watson
10 Biemann separators; jet separators; and molecular separating membranes. These methods provide differing degrees of sample enrichment, but none provide 100% sample transmission.

15 Watson Biemann separators are based on the concept of enrichment by diffusion. The lighter carrier gas molecules permeate an effusion barrier, such as sintered glass, in preference to the heavier organic sample molecules and can be removed by a vacuum system. Although the separation procedure
20 does increase the sample-to-carrier gas ratio approximately 50 times, less than 50% of the sample passes into the mass spectrometer, resulting in a decrease in sensitivity due to the smaller sample size.

25 A precisely aligned, supersonic jet/orifice system may also be used to remove the carrier gas using the effusion principle. As the gas chromatograph effluent passes through a small jet, the stream is directed toward an orifice. The
30 concentration of carrier gas increases away from the center line while the concentration of the sample tends to increase toward the center. The orifice intercepts only the center portion of the stream.

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Two such jet/orifice assemblies may be used in series if desired. Using this method, approximately 60% of the sample is transmitted to the mass spectrometer with a sample enrichment of approximately 100.

05 Molecular membrane separators take advantage of differences in the permeability rate of the sample and the carrier gas through a silicone rubber membrane. The column effluent from the gas chromatograph passes a thin rubber membrane. The
10 carrier gas usually has a low permeability and is not adsorbed by the membrane, whereas the organic molecules are adsorbed and pass through the membrane and directly into the high vacuum of the mass spectrometer. Sample transmission rates vary between
15 50 and 90 percent, and the enrichment factor is approximately 1000.

 Another technique is disclosed in U. S. Patent No. 3,896,661 to Parkhurst et al which proposes the use of thin layer chromatography of the
20 mixture to be analyzed. The organic portion of the effluent of a gas chromatograph is placed on a chromatographic medium. The sample components migrate at different rates on the medium. The medium is then selectively heated to sublime the adsorbed
25 chemical substance directly into the ion source of the mass spectrometer. U. S. Patent No. 4,267,457 to Nakagawa et al shows a similar system in which a sample holding element is composed of a porous and gas permeable aggregate of ingredients which allow
30 the components of a sample to separate to form a chromatogram.

The systems of the above noted patents do not use a gas chromatograph and thus do not deal with

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the interface between a gas chromatograph and a mass spectrometer. Indeed, the separation of the sample components does not utilize the precise separation capabilities of a gas chromatograph in connection with a mass spectrometer to enhance the analysis of the sample.

The second noted problem which arises when interfacing gas chromatographs to mass spectrometers is the small time interval that may exist between two or more components in the gas chromatograph effluent. If the time required for scanning over the mass range of interest is longer than the time between the chromatograph peaks, the resulting mass spectrum is a mixture of the components. In the case of high resolution, capillary column gas chromatographs, the time between peaks can be less than a second. This has limited the gas chromatograph/mass spectrometer performance for all types of mass spectrometers and made it impossible to take full advantage of the capabilities of the high resolution mass spectrometers when interfaced with a gas chromatograph.

Although the Fourier transform mass spectrometer is a fast scanning instrument (up to 100 scans/second), the use of this speed in capillary gas chromatograph interfacing is not practical for several reasons. First, mass resolution obtained under such fast scanning rates is poor. Second, the signal-to-noise ratio is low due to the lack of time for adequate signal averaging of each gas chromatograph peak. To achieve high resolution mass spectra, detection time in the order of one second is needed. For a good signal-to-noise ratio, signal

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averaging for a few seconds is desirable. A third, but less important, problem with this method is the lack of time for Fourier transformation and the necessity of a large storage module in which to "dump" all of the raw data for later transformation.

SUMMARY OF THE INVENTION

The present invention is directed to obtaining a mass spectrometer sample from the effluent of a gas chromatograph. The sample obtained is essentially devoid of any carrier gas. The present invention includes a recording medium located within a housing on which the sample portion of the effluent is frozen. The apparatus also includes a means for introducing the effluent from the gas chromatograph into the housing, a cooling means for lowering the temperature of the recording medium below the freezing point of the sample portion of the effluent and a pressure regulator for maintaining a positive pressure within the housing to facilitate removal of the carrier gas portion of the effluent. The recording medium is transported within the housing during the freezing process so that the different components of the sample are deposited upon different portions of the recording medium. In this way, the carrier gas is removed from the system so that the mass spectrometer can operate at a high vacuum.

To introduce the resultant, recorded sample into the mass spectrometer, the recording medium is first returned to its original position within the housing. The medium is once again moved, and a heater heats the recording medium so that the sample portion is evaporated from the recording medium. The

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sample is then pumped into the mass spectrometer. The recording medium may be moved at a rate dependent on the scanning time of the mass spectrometer which makes the sample introduction rate independent of the time interval between the peaks or components in the gas chromatograph effluent.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a cut-away view of a portion of the present invention.

FIG. 2 shows a preferred embodiment of the present invention incorporating the portion illustrated in FIG. 1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

FIG. 1 and FIG. 2 show gas chromatograph/mass spectrometer interface cassette designated generally at 8. A housing 10 is constructed of a non-magnetic material, such as stainless steel. A metal tape 12, such as stainless steel, is wound on and between a supply reel 14 and a takeup reel 16. The diameters of reels 14 and 16 are relatively large as compared to the thickness of the tape to lessen the effect of the change of radius as the tape 12 is wrapped or unwrapped over the reels and itself. The reels 14 and 16 are constructed of aluminum or other non-magnetic material and carry iron bars 18, for reason to be described below. Non-magnetic tape guide rollers 20 direct the movement of the tape within the housing.

Movement of the metal tape 12 between supply reel 14 and takeup reel 16 is controlled by an external motor 22 (see FIG. 2). The motor 22 drives a magnet wheel 24 through an appropriate drive mechanism, such as belt 26 and associated pulleys.

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The magnet wheel 24 is positioned outside of the housing 10 and is magnetically coupled to the bars 18 of either the supply reel 14 or the takeup reel 16. The motor 22 can be a stepper motor under computer control for preprogrammed movement. Rotation of the magnet wheel will result in rotation of the associated reel and movement of the metal tape 12. A separate motor and drive may be provided for each magnet wheel 24.

Three gas connections are made with the interior of the housing 10. Purge gases, such as nitrogen or helium, are introduced into the housing 10 via purge gas port 28. The flow rate is controlled by valve 30. The pressure in the housing is lowered into the high vacuum range by evacuating housing 10 through vacuum port 32 using pump 34, which is operated by pump motor 36 and control valve 38. In addition, a high vacuum connector 40 is provided which is alternatively connected to either the gas chromatograph (not shown) or the mass spectrometer (not shown).

Care must be taken in the construction of the interface cassette 8 to ensure high vacuum performance. The cassette 8 can be made of 316 stainless steel or aluminum. No magnetic material should be used so as to avoid interference with the magnetic drive mechanism. However, other drives may permit the use of magnetic materials. Magnetic coupling is preferred in that it does not require a physical penetration of the cassette. The housing 10 and all joints and valves should be leak-proof and helium-tested to be certain that it can provide a vacuum of 10^{-10} torr or better. To avoid

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contamination, no lubricating materials with vapor pressure greater than 10^{-7} torr at room temperature should be used within the housing 10.

05 Before recording the gas chromatograph effluent, the metal tape 12 should be pre-cooled. This can be done conveniently by immersing the interface cassette 8 in liquid nitrogen 42 that is contained in a Dewar flask 44 having a suitable cover 46 (see FIG. 2). This environment will also allow
10 the interface cassette 8 to be kept cold during recording and after. To avoid water condensation on the cold metal tape and on the walls of the cassette, it is recommended that the cassette be purged with dry cold nitrogen or helium during cooling. This can
15 be done using the purge gas port 28 as a purge gas entrance and the high vacuum connector 40 as an exit. Vacuum port 32 is closed via the control valve 38 during the cool-down period.

20 During recording of the gas chromatograph effluent on the cold metal tape 12, the control valve 38 is open and purge gas is pumped out of cassette 8 through vacuum port 32 by operation of the pump 34. The outlet of the gas chromatograph column is then interconnected with the cassette 8 via high vacuum
25 connector 40. This interconnection can be either a direct connection to the connector 40 or by a proper transfer line. A slow gas purge through purge port 28 during the recording ensures a positive pressure within the housing 10 and prevents possible
30 contamination of the rest of the metal tape 10. That is, the positive pressure established through port 28 and the removal of gas through port 32, whose inlet is adjacent the connector 40, prevent or reduce the migration throughout the housing of effluent entering.

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through the connector 40. Additionally, the possibility of contamination may be further reduced by isolating the gas chromatograph effluent sample from the rest of the metal tape by use of a sample cell 48. The cell 48 has inlet and outlet apertures 50 which allow the metal tape 12 to move through the cell 48.

During recording, it may be desirable to keep the sample cell 48 warm or at room temperature to avoid condensation of the effluent sample on the walls of the cell 48 instead of the metal tape 12. If that is the case, a small heater 52 can be installed within the cell 48 and connected to appropriate electrical conductors 54.

After injection of the sample into the gas chromatograph, recording is started. The speed of the metal tape 12 during recording should be chosen based on the resolution and widths of the gas chromatograph peaks. Movement of the tape 12 is controlled by motor 22. During recording, organic compounds will freeze on the metal tape 12. The carrier gas has a much lower freezing point and does not freeze on the tape 12 and is pumped out through vacuum port 32. The recording continues until the sample has completely passed through the gas chromatograph. For example, if metal tape with a thickness of .001 inch wrapped on a 7 cm diameter reel, a wrapped thickness of 0.5 cm (a total diameter of reel and tape of 7.5 cm) will last for approximately 37 minutes of recording at a tape speed of 2 cm/second.

After the recording is completed, the metal tape 12 may be stored for an indefinite length of

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time as long as the interface cassette 8 is kept cold, such as in liquid nitrogen. During storage, purge gas valve 30 and control valve 38 should be closed and the high vacuum connector 40 should be blanked off.

In order to transfer the recorded sample to a mass spectrometer, the interface cassette must be connected to the mass spectrometer via the high vacuum connector 40. The housing 10 must first be pumped out using a roughing pump. Either port 28 or port 32 may be employed. After the internal pressure of the housing 10 reaches milli-torr range, it is pumped to ultra high vacuum. With valves 30 and 38 closed and the cassette 8 under high vacuum and cold, the metal tape 12 must be rolled back to supply reel 14. This can be done by connecting motor 22 to the magnetic wheel 24 associated with the supply reel 14 and rewinding the tape 12. If desired, two motors can be used in order to move the tape in both the forward and rewind directions.

The frozen sample on tape 12 can now be transferred to the mass spectrometer by moving the tape 12 at the proper speed and heating the tape 12 locally by use of heater 52. The heating causes the organic materials to evaporate off of the tape to be pumped into the mass spectrometer, through the high vacuum connector 40, for analysis. Sample pressure in the mass spectrometer source can be adjusted by controlling the current through the heater 52 and/or the speed of the tape. In addition, an adjustable time separation for analysis of different compounds can be obtained by controlling the movement of the tape.

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Obviously, many modifications and variations of the present invention are possible in light of the above teachings. For example, it may be desirable to put grooves on the tape 12 or to coat the back of the metal tape 12 with some non-volatile, non-stick material to prevent the transfer of frozen sample from one layer of wrapped tape 12 to the layer above. Also, the heating of the tape 12 to evaporate the sample can be done using a laser source. This allows multiple mass analyses of a single gas chromatograph run by only partially evaporating the sample and storing the rest. It should also be noted that the present invention also allows mass analysis of a single gas chromatograph run under different mass spectrometry conditions. This is possible by merely stopping the tape and changing the mass spectrometer parameters during or between each gas chromatograph peak. It is therefore to be understood that the present invention may be practiced otherwise than as specifically described.

CLAIMS:

1. Apparatus for obtaining a mass spectrometer sample from the effluent of a gas chromatograph, the sample being essentially devoid of any chromatograph carrier gas, the apparatus comprising:

recording means located within a housing;

means introducing the gas chromatograph

effluent into the housing;

cooling means lowering the temperature of the

recording medium for freezing the

non-carrier gas portion of the effluent

on the surface of the recording medium;

and

means for removing the carrier gas portion

of the effluent therefrom.

2. The apparatus of claim 1 wherein the housing is non-magnetic.

3. The apparatus of claim 1 wherein the recording means comprises a metal strip.

4. The apparatus of claim 1 wherein the recording means comprises a metal tape.

5. The apparatus of claim 4 wherein the metal tape is comprised of stainless steel.

6. The apparatus of claim 1, further comprising tape transport means.

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7. The apparatus of claim 6 wherein the tape transport means comprises:

tape supply and take-up roller means located within the housing, the roller means being non-magnetic; and
magnetic drive means for rotating the rollers.

8. The apparatus of claim 7 wherein the magnetic drive means comprises:

magnetic means affixed to the tape supply and take-up roller means; and
magnet means attached to motor means outside the housing for rotating the roller means without penetration of the housing.

9. The apparatus of claim 8 wherein the motor means is a variable speed stepper motor.

10. The apparatus of claim 1, further comprising means isolating a portion of the recording means from the remainder of the recording means within the housing.

11. The apparatus of claim 10 wherein the isolating means comprises:

sample cell means for receiving the effluent from the gas chromatograph; and
entrance and exit aperture means in the sample cell for passing a portion of the recording means through the sample cell.

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12. The apparatus of claim 11 further comprising:
vacuum means interfaced with the sample cell
for lowering the pressure within the
sample cell.
13. The apparatus of claim 12 wherein the vacuum
means comprises a pump.
14. The apparatus of claim 11 further comprising:
means for interfacing the sample cell means
with a mass spectrometer.
15. The apparatus of claim 1, further comprising
heating means.
16. The apparatus of claim 15 wherein the
heating means is a filament.
17. The apparatus of claim 15 wherein the
heating means is a laser.
18. The apparatus in claim 1 further comprising
pressure regulating means for maintaining a positive
pressure within the housing which includes purge gas
means.
19. The apparatus in claim 18 wherein the purge
gas means comprises nitrogen gas.
20. The apparatus in claim 18 wherein the purge
gas means comprises helium gas.

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21. A method for obtaining a mass spectrometer sample from the effluent of a gas chromatograph, the sample being essentially devoid of any chromatograph carrier gas, the method comprising the steps of:

- cooling a metal tape within a housing;
- purging moisture from the housing;
- connecting the housing to the output of the gas chromatograph;
- injecting a specimen into the gas chromatograph;
- freezing a portion of the chromatograph effluent on the surface of the metal tape; and
- removing the carrier gas from the housing.

22. The method of claim 21 further comprising the step of moving the tape at a first predetermined speed.

23. The method of claim 21 wherein the step of moving the tape comprises the step of moving the tape from a supply reel to a take-up reel and the steps of:

- rewinding the metal tape from the take-up reel to the supply reel;
- connecting the housing to the input of the mass spectrometer;
- moving the tape at a second predetermined speed from the supply reel to the take-up reel;
- heating a portion of the metal tape so that the sample evaporates from the tape; and
- delivering the sample into the mass spectrometer.

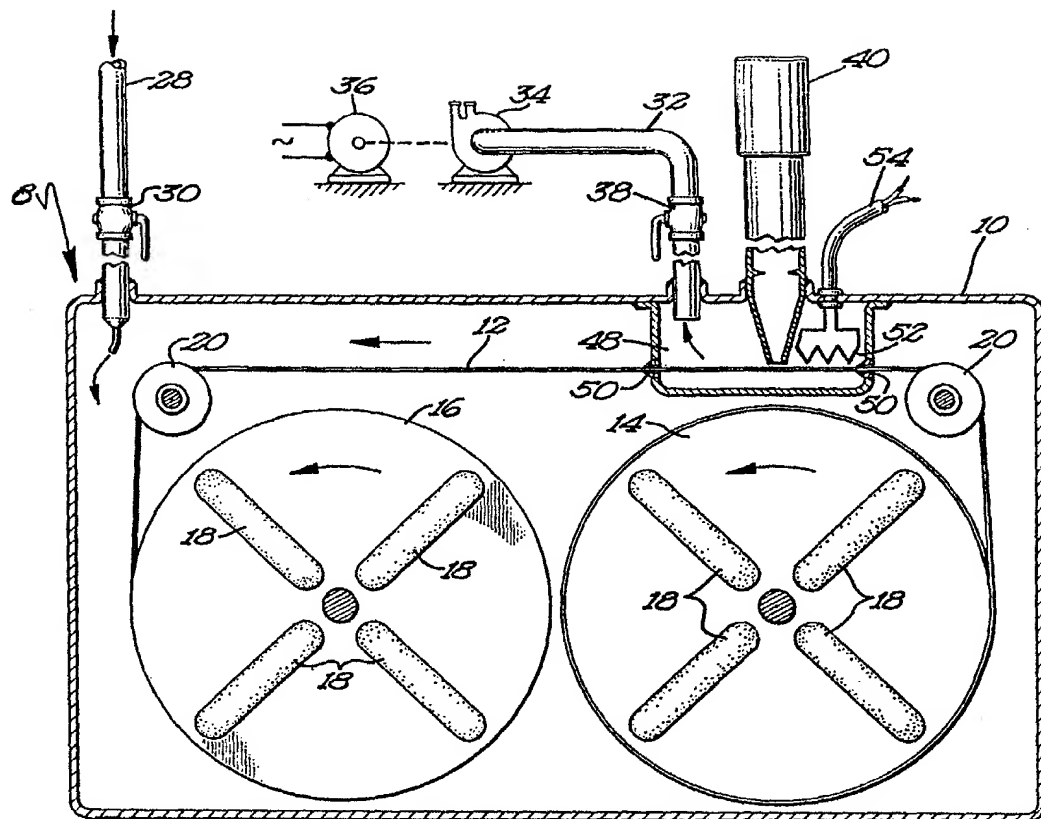


Fig 1

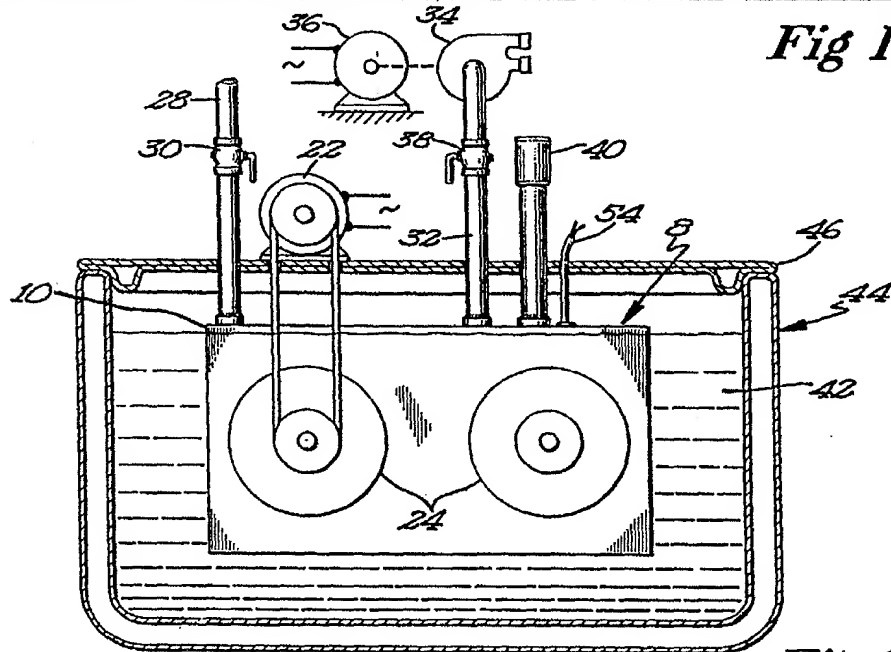


Fig 2



European Patent
Office

EUROPEAN SEARCH REPORT

0175467

Application number

EP 85 30 5608

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	G.I.T. FACHZEITSCHRIFT FÜR DAS LABORATORIUM, vol. 11, 15Jg, November 1971, pages 1234-1238, DE; R. LETTERER: "Direkte Kopplung Gaschromatograph-Massenspektrometer über eine Ausfriervorrichtung" * Whole document * ---	1	G 01 N 30/84 G 01 N 30/72
Y	US-A-3 592 044 (D.E. GREEN) * Whole document * ---	1	
A	US-A-3 957 470 (E.F. DAWES) * Whole document * ---	1	
A	US-A-3 589 171 (F.C. HALEY) * Whole document * ---	1	
A	US-A-3 912 470 (R. FLUCKIGER) * Whole document * ---	1	
A	US-A-3 712 111 (P.M. LLEWELLYN) * Whole document * -----	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 06-12-1985	Examiner CALLEWAERT-HAEZEBROU
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	



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(56) References cited:
**US-A-3 589 171
US-A-3 592 044
US-A-3 712 111
US-A-3 912 470
US-A-3 957 470**

**G.I.T. FACHZEITSCHRIFT FÜR DAS
LABORATORIUM, vol. 11, 15Jg, November 1971,
pages 1234-1238, DE; R. LETTERER: "Direkte
Kopplung Gaschromatograph-
Massenspektrometer über eine
Ausfriervorrichtung"**

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Courier Press, Leamington Spa, England.

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Description

The present invention relates to the preparation of a mass spectrometer sample from the effluent of a gas chromatograph.

Gas chromatography is very useful as a separator of compounds, while a mass spectrometer is an excellent instrument for identifications. An effective interface would allow each instrument to operate in sequence, without degrading the performance of either. By separating the components of a specimen in a gas chromatograph, more accurate determinations with a mass spectrometer appear possible. However, interfacing a gas chromatograph with a mass spectrometer presents two problems: (1) separation of the sample from the chromatograph carrier gas; and (2) the time between the different chromatograph peaks as they reach the mass spectrometer as compared to the necessary or desired scanning time of the spectrometer.

The first problem noted above arises from the fact that gas chromatographs normally operate at pressures greater than 101 kPa (760 torr), while mass spectrometers function best at high vacuums in the 1.33×10^{-6} kPa (10^{-5} torr) range, or greater. Fourier Transform mass spectrometers operate optimally near 1.33×10^{-9} kPa (10^{-8} torr). Thus, an interface between a gas chromatograph and a mass spectrometer has required a "throwing away" of some or most of the sample, with the resultant loss of sample size sensitivity. This problem is even more pronounced with packed column gas chromatographs due to the higher quantity of carrier gas in the column which must be removed before the sample can be introduced into the mass spectrometer.

The second noted problem which arises when interfacing gas chromatographs to mass spectrometers is the small time interval that may exist between two or more components in the gas chromatograph effluent. If the time required for scanning over the mass range of interest is longer than the time between the chromatograph peaks, the resulting mass spectrum is a mixture of the components. In the case of high resolution, capillary column gas chromatographs, the time between peaks can be less than a second. This has limited the gas chromatograph/mass spectrometer performance for all types of mass spectrometers and made it impossible to take full advantage of the capabilities of the high resolution mass spectrometers when interfaced with a gas chromatograph.

Although the Fourier transform mass spectrometer is a fast scanning instrument (up to 100 scans/second), the use of this speed in capillary gas chromatograph interfacing is not practical for several reasons. First, mass resolution obtained under such fast scanning rates is poor. Second, the signal-to-noise ratio is low due to the lack of time for adequate signal averaging of each gas chromatograph peak. To achieve high resolution mass spectra, detection time in the order of one second is needed. For a good signal-to-noise

ratio, signal averaging for a few seconds is desirable. A third, but less important, problem with this method is the lack of time for Fourier transformation and the necessity of a large storage module in which to "dump" all of the raw data for later transformation.

U.S. Patent Specification No. 3,592,044 describes a system in which the effluent from a gas chromatograph is passed through a tube which is cooled so that the sample components are deposited on the walls of the tube while the carrier gas passes through and is removed to exhaust. The sample is subsequently vapourized for delivery to a mass spectrometer.

G.I.T. Fachzeitschrift für das Laboratorium, vol. 11, 15. Jg., November 1971, pages 1234-1238, DE: R. Letterer: "Direkte Kopplung Gaschromatograph-Massenspektrometer über eine Ausfreivorrichtung" also describes a system in which a cold trap is used as an interface between a gas chromatograph and a mass spectrometer.

In comparison with the known apparatus for obtaining a mass spectrometer sample from the effluent of a gas chromatograph, which comprises a receiving surface located within a housing, and cooling means for the receiving surface to cause deposition of the sample from the effluent onto the surface while allowing the carrier gas to pass through the housing, the present invention is characterized in that the receiving surface is on a recording medium which is transportable within the housing to present fresh areas of receiving surface for successive portions of the sample.

In the embodiment to be described the apparatus includes a recording medium located within a housing on which the sample portion of the effluent is frozen. The apparatus also includes a means for introducing the effluent from the gas chromatograph into the housing, a cooling means for lowering the temperature of the recording medium below the freezing point of the sample portion of the effluent and a pressure regulator for maintaining a positive pressure within the housing to facilitate removal of the carrier gas portion of the effluent. The recording medium is transported within the housing during the freezing process so that the different components of the sample are deposited upon different portions of the recording medium. In this way, the carrier gas is removed from the system so that the mass spectrometer can operate at a high vacuum.

To introduce the resultant, recorded sample into the mass spectrometer, the recording medium is first returned to its original position within the housing. The medium is once again moved, and a heater heats the recording medium so that the sample portion is evaporated from the recording medium. The sample is then pumped into the mass spectrometer. The recording medium may be moved at a rate dependent on the scanning time of the mass spectrometer which makes the sample introduction rate independent of the time interval between the peaks or components in the gas chromatograph effluent.

Furthermore, the present invention also comprises a method as disclosed in claim 9.

Brief description of the drawings

Figure 1 shows a cut-away view of a portion of the present invention.

Figure 2 shows a preferred embodiment of the present invention incorporating the portion illustrated in Figure 1.

Detailed description of the preferred embodiment

Figure 1 and Figure 2 show gas chromatograph/mass spectrometer interface cassette designated generally at 8. A housing 10 is constructed of a non-magnetic material, such as stainless steel. A metal tape 12, such as stainless steel, is wound on and between a supply reel 14 and a takeup reel 16. The diameters of reels 14 and 16 are relatively large as compared to the thickness of the tape to lessen the effect of the change of radius as the tape 12 is wrapped or unwrapped over the reels and itself. The reels 14 and 16 are constructed of aluminum or other non-magnetic material and carry iron bars 18, for reason to be described below. Non-magnetic tape guide rollers 20 direct the movement of the tape within the housing.

Movement of the metal tape 12 between supply reel 14 and takeup reel 16 is controlled by an external motor 22 (see Figure 2). The motor 22 drives a magnet wheel 24 through an appropriate drive mechanism, such as belt 26 and associated pulleys.

The magnet wheel 24 is positioned outside of the housing 10 and is magnetically coupled to the bars 18 of either the supply reel 14 or the takeup reel 16. The motor 22 can be a stepper motor under computer control for preprogrammed movement. Rotation of the magnet wheel will result in rotation of the associated reel and movement of the metal tape 12. A separate motor and drive may be provided for each magnet wheel 24.

Three gas connections are made with the interior of the housing 10. Purge gases, such as nitrogen or helium, are introduced into the housing 10 via purge gas port 28. The flow rate is controlled by valve 30. The pressure in the housing is lowered into the high vacuum range by evacuating housing 10 through vacuum port 32 using pump 34, which is operated by pump motor 36 and control valve 38. In addition, a high vacuum connector 40 is provided which is alternatively connected to either the gas chromatograph (not shown) or the mass spectrometer (not shown).

Care must be taken in the construction of the interface cassette 8 to ensure high vacuum performance. The cassette 8 can be made of 316 stainless steel or aluminum. No magnetic material should be used so as to avoid interference with the magnetic drive mechanism. However, other drives may permit the use of magnetic materials. Magnetic coupling is preferred in that it does not require a physical penetration of the cassette. The housing 10 and all joints and valves should be leak-proof and

helium-tested to be certain that it can provide a vacuum of 1.33×10^{-11} kPa (10^{-10} torr) or better. To avoid contamination, no lubricating materials with vapor pressure greater than 1.33×10^{-8} kPa (10^{-7} torr) at room temperature should be used within the housing 10.

Before recording the gas chromatograph effluent, the metal tape 12 should be pre-cooled. This can be done conveniently by immersing the interface cassette 8 in liquid nitrogen 42 that is contained in a Dewar flask 44 having a suitable cover 46 (see Figure 2). This environment will also allow the interface cassette 8 to be kept cold during recording and after. To avoid water condensation on the cold metal tape and on the walls of the cassette, it is recommended that the cassette be purged with dry cold nitrogen or helium during cooling. This can be done using the purge gas port 28 as a purge gas entrance and the high vacuum connector 40 as an exit. Vacuum port 32 is closed via the control valve 38 during the cool-down period.

During recording of the gas chromatograph effluent on the cold metal tape 12, the control valve 38 is open and purge gas is pumped out of cassette 8 through vacuum port 32 by operation of the pump 34. The outlet of the gas chromatograph column is then interconnected with the cassette 8 via high vacuum connector 40. This interconnection can be either a direct connection to the connector 40 or by a proper transfer line. A slow gas purge through purge port 28 during the recording ensures a positive pressure within the housing 10 and prevents possible contamination of the rest of the metal tape 10. That is, the positive pressure established through port 28 and the removal of gas through port 32, whose inlet is adjacent the connector 40, prevent or reduce the migration throughout the housing of effluent entering through the connector 40. Additionally, the possibility of contamination may be further reduced by isolating the gas chromatograph effluent sample from the rest of the metal tape by use of a sample cell 48. The cell 48 has inlet and outlet apertures 50 which allow the metal tape 12 to move through the cell 48.

During recording, it may be desirable to keep the sample cell 48 warm or at room temperature to avoid condensation of the effluent sample on the walls of the cell 48 instead of the metal tape 12. If that is the case, a small heater 52 can be installed within the cell 48 and connected to appropriate electrical conductors 54.

After injection of the sample into the gas chromatograph, recording is started. The speed of the metal tape 12 during recording should be chosen based on the resolution and widths of the gas chromatograph peaks. Movement of the tape 12 is controlled by motor 22. During recording, organic compounds will freeze on the metal tape 12. The carrier gas has a much lower freezing point and does not freeze on the tape 12 and is pumped out through vacuum port 32. The recording continues until the sample has completely passed through the gas chromatograph.

For example, if metal tape with a thickness of 2.54×10^{-3} cm (.001 inch) wrapped on a 7 cm diameter reel, a wrapped thickness of 0.5 cm (a total diameter of reel and tape of 7.5 cm) will last for approximately 37 minutes of recording at a tape speed of 2 cm/second.

After the recording is completed the metal tape 12 may be stored for an indefinite length of time as long as the interface cassette 8 is kept cold, such as in liquid nitrogen. During storage, purge gas valve 30 and control valve 38 should be closed and the high vacuum connector 40 should be blanked off.

In order to transfer the recorded sample to a mass spectrometer, the interface cassette must be connected to the mass spectrometer via the high vacuum connector 40. The housing 10 must first be pumped out using a roughing pump. Either port 28 or port 32 may be employed. After the internal pressure of the housing 10 reaches 10^{-4} kPa (milli-torr) range, it is pumped to ultra high vacuum. With valves 30 and 38 closed and the cassette 8 under high vacuum and cold, the metal tape 12 must be rolled back to supply reel 14. This can be done by connecting motor 22 to the magnetic wheel 24 associated with the supply reel 14 and rewinding the tape 12. If desired, two motors can be used in order to move the tape in both the forward and rewind directions.

The frozen sample on tape 12 can now be transferred to the mass spectrometer by moving the tape 12 at the proper speed and heating the tape 12 locally by use of heater 52. The heating causes the organic materials to evaporate off of the tape to be pumped into the mass spectrometer, through the high vacuum connector 40, for analysis. Sample pressure in the mass spectrometer source can be adjusted by controlling the current through the heater 52 and/or the speed of the tape. In addition, an adjustable time separation for analysis of different compounds can be obtained by controlling the movement of the tape.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. For example, it may be desirable to put grooves on the tape 12 or to coat the back of the metal tape 12 with some non-volatile, non-stick material to prevent the transfer of frozen sample from one layer of wrapped tape 12 to the layer above. Also, the heating of the tape 12 to evaporate the sample can be done using a laser source. This allows multiple mass analyses of a single gas chromatograph run by only partially evaporating the sample and storing the rest. It should also be noted that the present invention also allows mass analysis of a single gas chromatograph run under different mass spectrometry conditions. This is possible by merely stopping the tape and changing the mass spectrometer parameters during or between each gas chromatograph peak. It is therefore to be understood that the present invention may be practiced otherwise than as specifically described.

Claims

1. Apparatus for obtaining a mass spectrometer sample from the effluent of a gas chromatograph, comprising a receiving surface (12) located within a housing (8), cooling means (42) for the receiving surface to freeze the sample from the effluent onto the surface and means (28) for removing from the housing carrier gas from which the sample has been removed characterized in that the receiving surface is on a recording medium (12) which is transportable within the housing to present fresh areas of receiving surface for successive portions of the sample.

2. Apparatus as claimed in Claim 1 characterized in that the recording medium is a metal strip or tape (12) and the housing contains tape supply and take-up rollers (14, 16) between which the tape is transportable.

3. Apparatus as claimed in Claim 2 in which the metal strip or tape is composed of stainless steel.

4. Apparatus as claimed in Claim 2 or 3 characterized by a magnetic drive means (18, 24) for rotation of the rollers from outside the housing in order to transport the recording medium.

5. Apparatus as claimed in Claim 4 in which the magnetic drive means includes a variable speed stepper motor (24) outside the housing.

6. Apparatus as claimed in any of the preceding claims characterized by a sample cell (48) within the housing (8), a chromatographic effluent inlet (40) to the sample cell and an outlet (32) for removal of carrier gas from the sample cell, the recording medium passing through the sample cell.

7. Apparatus as claimed in Claim 6, characterized by an inlet (28) for purge gas to the housing outside the sample cell to enable a positive pressure to be maintained between the housing and the sample cell.

8. Apparatus as claimed in Claim 6 or 7 characterized by a heater (52) for maintaining the wall of the sample cell at a temperature above that of the recording medium.

9. A method of obtaining a mass spectrometer sample from the effluent of a gas chromatograph in which the effluent is passed over a cooled surface in a housing from which moisture has been purged and the sample is frozen onto the cooled surface while the carrier gas is removed characterized in that the cooled surface on which the sample is frozen is that of a recording medium which is transported through the zone of freezing.

10. A method as claimed in Claim 9 in which the recording medium is in the form of a metal tape transportable between a supply reel and a take-up reel contained within a housing and cooling of the deposition surface is effected by immersing the housing in a refrigerated bath.

11. A method as claimed in Claim 9 or 10 characterized in that the frozen sample is subsequently vaporized for delivery to the mass spectrometer by transporting the recording medium through a vaporization zone.

12. A method as claimed in Claim 10 charac-

terized in that the tape is re-wound from the take-up reel to the supply reel after deposition of the sample and the frozen sample is subsequently vaporized for delivery to the mass spectrometer by transporting the tape through a vaporization zone from the supply reel to the take-up reel.

13. A method as claimed in Claim 11 or 12 in which the vaporization zone is the same as the deposition zone.

Patentansprüche

1. Vorrichtung zum Erhalten einer Massenspektrometerprobe vom Ausfluß eines Gaschromatographen mit einer Aufnahme­fläche (12), die in einem Gehäuse (8) angeordnet ist, einer Kühleinrichtung (42) für die Aufnahme­fläche zum Gefrieren der Probe aus dem Ausfluß auf die Fläche und einer Einrichtung (28) zum Entfernen von Trägergas aus dem Gehäuse, aus dem die Probe entfernt worden ist, dadurch gekennzeichnet, daß sich die Aufnahme­fläche auf einem Aufzeichnungsmedium (12) befindet, das im Gehäuse transportierbar ist, um frische Bereiche der Aufnahme­fläche aufeinanderfolgenden Teilen der Probe zur Verfügung zu stellen.

2. Vorrichtung nach Anspruch 1, dadurch gekennzeichnet, daß es sich bei dem Aufzeichnungsmedium um einen Metallstreifen oder ein Metallband (12) handelt und daß das Gehäuse Bandzuführ- und -aufnahmerollen (14, 16) enthält, zwischen denen das Band förderbar ist.

3. Vorrichtung nach Anspruch 2, bei der der Metallstreifen oder das Metallband aus rostfreiem Stahl besteht.

4. Vorrichtung nach Anspruch 2 oder 3, gekennzeichnet, durch eine magnetische Antriebseinrichtung (18, 24) zur Drehung der Rollen von der Außenseite des Gehäuses, um das Aufzeichnungsmedium zu fördern.

5. Vorrichtung nach Anspruch 4, bei der die magnetische Antriebseinrichtung einen Schrittmotor (24) mit veränderlicher Drehzahl außerhalb des Gehäuses umfaßt.

6. Vorrichtung nach einem der vorangehenden Ansprüche, gekennzeichnet, durch eine Probenzelle (48) im Gehäuse (8), einen Einlaß (40) für den chromatographischen Ausfluß zur Probenzelle und einen Auslaß (32) zum Entfernen des Trägergases von der Probenzelle, wobei sich das Aufzeichnungsmedium durch die Probenzelle erstreckt.

7. Vorrichtung nach Anspruch 6, gekennzeichnet, durch einen Einaß (28) für Reinigungsgas für das Gehäuse außerhalb der Probenzelle, so daß ein positiver Druck zwischen dem Gehäuse und der Probenzelle aufrechterhalten werden kann.

8. Vorrichtung nach Anspruch 6 oder 7, gekennzeichnet, durch eine Heizeinrichtung (52) zum Halten der Wand der Probenzelle auf einer Temperatur über der des Aufzeichnungsmediums.

9. Verfahren zum Erhalten einer Massenspektrometerprobe vom Ausfluß eines Gaschromatographen, bei dem der Ausfluß über eine gekühlte Fläche in einem Gehäuse, aus dem Feuchtigkeit

entfernt worden ist, geleitet und die Probe auf die gekühlte Fläche gefroren wird, während das Trägergas entfernt wird, dadurch gekennzeichnet, daß die gekühlte Fläche, auf die die Probe gefroren wird, die eines Aufzeichnungsmediums ist, das durch die Gefrierzone gefördert wird.

10. Verfahren nach Anspruch 9, bei dem das Aufzeichnungsmedium die Form eines Metallbandes besitzt, das zwischen einer Zuführspule und einer Aufnahmespule, die im Gehäuse angeordnet sind, förderbar ist und daß das Kühlen der Aufnahme­fläche durch Eintauchen des Gehäuses in ein tiefgekühltes Bad bewirkt wird.

11. Verfahren nach Anspruch 9 oder 10, dadurch gekennzeichnet, daß die gefrorene Probe danach zur Zuführung zum Massenspektrometer durch Fördern des Aufzeichnungsmediums durch eine Verdampfungszone verdampft wird.

12. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß das Band von der Aufnahmespule wieder auf die Zuführspule gewickelt wird, nachdem die Probe abgelagert worden ist und die gefrorene Probe danach zur Abgabe an das Massenspektrometer durch Fördern des Bandes durch eine Verdampfungszone von der Zuführspule zur Aufnahmespule verdampft worden ist.

13. Verfahren nach Anspruch 11 oder 12, bei dem die Verdampfungszone der Ablagerungszone entspricht.

Revendications

1. Dispositif permettant d'obtenir un échantillon d'un spectromètre de masse à partir de l'effluent d'un chromatographe à gaz, comprenant une surface réceptrice (12) située à l'intérieur d'un boîtier (8), des moyens de refroidissement (42) pour la surface réceptrice, servant à geler l'échantillon provenant de l'effluent sur la surface, et des moyens (28) pour éliminer du boîtier le gaz porteur, dont l'échantillon a été retiré, caractérisé en ce que la surface réceptrice est disposée sur un support d'enregistrement (12), qui est transportable à l'intérieur du boîtier de manière à présenter de nouvelles zones de la surface réceptrice à des parties successives de l'échantillon.

2. Dispositif selon la revendication 1, caractérisé en ce que le support d'enregistrement est un ruban ou une bande métallique (12) et que le boîtier contient des galets (14, 16) de dévidage et de rembobinage de la bande, entre lesquels la bande peut être déplacée.

3. Dispositif selon la revendication 2, dans lequel le ruban ou la bande métallique est réalisé en un acier inoxydable.

4. Dispositif selon la revendication 2 ou 3, caractérisé par des moyens d'entraînement magnétiques (18, 24) servant à faire tourner les galets à partir de l'extérieur du boîtier de manière à entraîner le support d'enregistrement.

5. Dispositif selon la revendication 4, dans lequel les moyens d'entraînement magnétiques comprennent un moteur pas-à-pas à vitesse variable (24) situé à l'extérieur du boîtier.

6. Dispositif selon l'une quelconque des revendications précédentes, caractérisé par une cellule à échantillon (48) à l'intérieur du boîtier (8), une entrée (40) pour l'effluent chromatographique aboutissant à la cellule à échantillon et une sortie (32) pour l'élimination du gaz porteur de la cellule à échantillon, le support d'enregistrement traversant la cellule à échantillon.

7. Dispositif selon la revendication 6, caractérisé par une entrée (28) pour le gaz de purge envoyé au boîtier et situé à l'extérieur de la cellule à échantillon de manière à permettre le maintien d'une pression positive entre le boîtier et la cellule à échantillon.

8. Dispositif selon la revendication 6 ou 7, caractérisé par un dispositif de chauffage (52) servant à maintenir la paroi de la cellule à échantillon à une température supérieure à celle du support d'enregistrement.

9. Procédé pour obtenir un échantillon d'un spectromètre de masse à partir de l'effluent d'un chromatographe à gaz, dans lequel cet effluent circule sur une surface refroidie à l'intérieur d'un boîtier, dont l'humidité a été évacuée, et l'échantillon est gelé sur la surface refroidie, tandis que le gaz porteur est retiré, caractérisé en ce que la surface refroidie, sur laquelle l'échantillon est gelé, est celle d'un support

d'enregistrement, qui est entraîné à travers la zone de congélation.

10. Procédé selon la revendication 9, dans lequel le support d'enregistrement se présente sous la forme d'une bande métallique pouvant être transportée entre une bobine débitrice et une bobine réceptrice, logées à l'intérieur d'un boîtier, et le refroidissement de la surface de dépôt est réalisé par immersion du boîtier dans un bain réfrigéré.

11. Procédé selon la revendication 9 ou 10, caractérisé en ce que l'échantillon gelé est ensuite vaporisé de manière à être envoyé au spectromètre de masse, grâce au transport du support d'enregistrement à l'intérieur d'une zone de vaporisation.

12. Procédé selon la revendication 10, caractérisé en ce que la bande est rembobinée à partir de la bobine réceptrice sur la bobine débitrice après le dépôt de l'échantillon, et l'échantillon gelé est ensuite vaporisé de manière à être envoyé au spectromètre de masse, sous l'effet du transport de la bande à travers une zone de vaporisation depuis la bobine débitrice en direction de la bobine réceptrice.

13. Procédé selon la revendication 11 ou 12, dans lequel la zone de vaporisation constitue la zone de dépôt.

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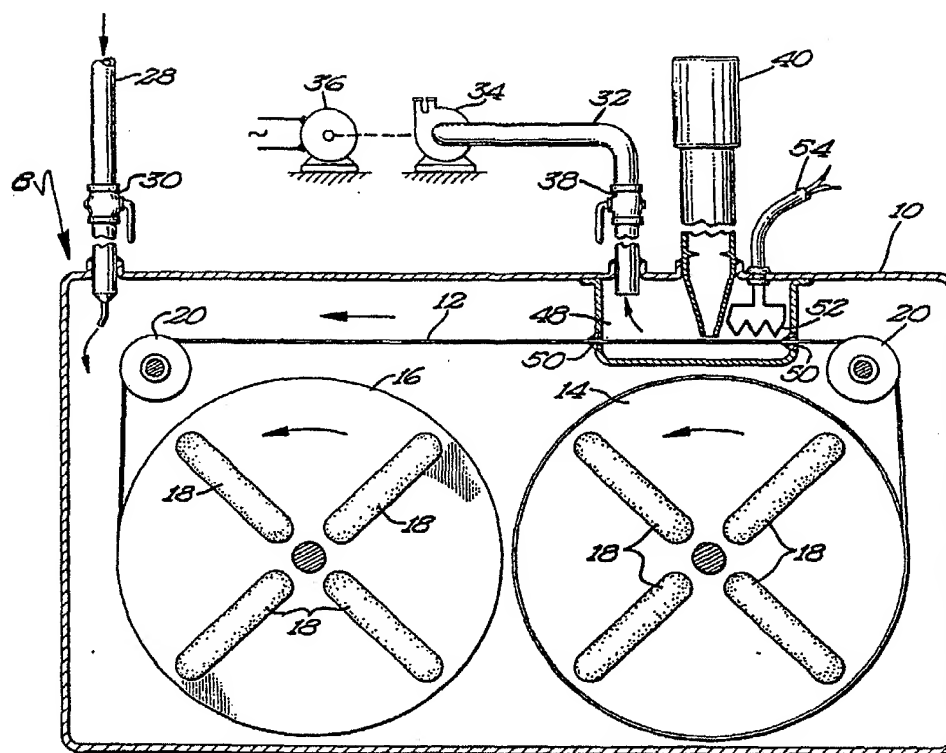


Fig 1

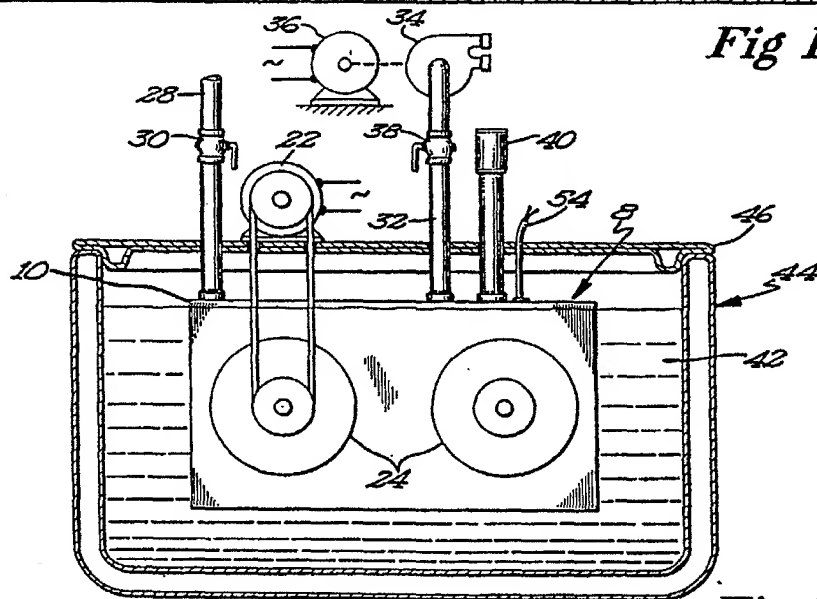


Fig 2